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DOCUMENT-IDENTIFIER: US 6177181 B1
TITLE: Porous films, process for producing the same, and laminate films and recording sheets made with the use of the porous films

Abstract Text (1)
Porous membranes having a micro phase separation structure and showing a light transmittance at the wavelength of 400 nm of not less than 30% are obtained by the dry phase [illegible] method comprising drying a coating layer of a dope containing a [illegible] solvent for the polymer and a poor solvent for the polymer which [illegible] higher boiling point than the good solvent. The polymer includes cellulose derivatives, vinyl-series polymers such as acrylonitrile-series polymers and (meth)acrylic acid ester-series polymers, polysulfone-series polymers, and the like. The porous polymer membranes have a porosity of 10 to 60%, a mean pore size of about 0.005 to 0.25 .mu.m and a maximum pore size of not greater than [illegible] .mu.m. These porous membranes shows not only excellent transparency but also high productivity.

Brief Summary Text (2):
The present invention relates to a porous membrane made of a polymer and excellent in transparency, a laminate film having the porous membrane and a process for producing the porous membrane.

Brief Summary Text (4):
Since the creation of unsymmetric cellulose acetate membranes in 1960, there have been rapid developments in the field of porous polymer membranes and the fields of their application have been widening almost unlimitedly, for example in water purification to obtain ultrapure water, drinking water and industrial water, treatment of industrial waste water and municipal sewage, separation and purification of substances in various steps in chemical, pharmaceutical and food industries, and use in medical areas, typically in blood dialysis using artificial kidneys. Such porous polymer membranes mostly have a nonsymmetric structure composed of a skin layer (dense layer) and a [illegible] porous layer, and are generally opaque. As regards the use of porous polymer membranes in areas where transparency is required, Japanese Patent Application Laid-open No. 48[illegible] 1989 (JP-A-1-48[illegible]26), for instance, proposes liquid crystal panels comprising a transparent porous film impregnated with liquid crystal molecules and sandwiched between two panels. This reference, however, gives no mention of the material of the transparent porous film.

Brief Summary Text (7):
In Japanese Patent Application Laid-open No. 145005/1991 (JP-A-3-145005), a thin electrolyte membrane is proposed which comprises a porous solid polymer membrane having independent through holes with a mean diameter of 0.01 to 0.7 .mu.m, with the holes being filled with an ionic conductor material. This porous solid polymer membrane is produced by irradiating a thin polymer membrane with charged particles and etching the tracks of the charged particles with an alkali to form pores. The porous membrane obtained by this method is semitransparent. For rendering it transparent, it is necessary to fill the pores with a liquid having a refractive index approximately equal to that of the membrane material.

Brief Summary Text (9):
In Japanese Patent Application Laid-open No. [illegible] 1994 (JP-A-[illegible]), a recording sheet is disclosed which is a laminate comprising a substrate film layer, a [illegible] layer formed on at least one side of the substrate film layer, and a [illegible] layer (a polyethylene or polypropylene film with a large [illegible] having a diameter of [illegible] .mu.m formed therein) bonded to the liquid-absorbing layer by means of a hot press. However, no description is given of the

method of preparing the porous, thin membrane layer.

Brief Summary Text (12):
However, the phase separation method generally gives nonsymmetric membranes [illegible] a dense surface layer and a porous underlying layer [illegible]. The [illegible] layer has a large pore size, opacifying the porous membranes. If transparent membranes are formed, they will be nonporous membranes [illegible] in the [illegible] where [illegible]. It is thus difficult to obtain membranes or films having a porous [illegible] while retaining high transparency.

Brief Summary Text (13):
[illegible] an object of the present invention to provide highly transparent porous membranes and a process for producing the same.

Brief Summary Text (14):
Another object of the invention is to provide porous membranes high in transparency and ink absorption and excellent in water resistance, and a process for producing the same.

Brief Summary Text (15):
A further object of the invention is to provide a process for producing highly transparent porous membranes with high productivity.

Brief Summary Text (17):
To accomplish the above objects, the present inventors made intensive investigations paying particular attention to the dry phase conversion method which is outstanding, among the methods of producing porous polymer membranes, in effectiveness in mass production and, as a result, found that when a specific combination of solvents is employed, porous polymer membranes with remarkable transparency can be obtained. This finding has now led to completion of the present invention.

Brief Summary Text (18):
The porous membrane of the present invention comprises a polymer and shows a light transmittance of not less than 30% at the wavelength of 400 nm. This porous membrane usually has a micro phase separation structure. In the porous membrane, the mean size of pores may be 0.002 to 0.35 .mu.m, the maximum pore size may be about 0.4 .mu.m, and the porosity may be about 10 to 60%. The polymer includes various polymers, for example cellulose derivatives (e.g. cellulose esters such as cellulose acetate with a degree of acetylation of 42 to 62% and a viscosity average polymerization degree of 50 to 800), vinyl-series polymers (meth)acrylonitrile-series polymers, (meth)acrylic polymers, etc.), polysulfone-series polymers and so on. The porous membrane of the present invention also includes a porous membrane (A) comprising a polymer and having (B1) a porosity of 10 to 60% or (B2) pores having a mean pore size of 0.002 to 0.35 .mu.m, with the maximum pore size being not more than 0.4 .mu.m, and (C) showing a light transmittance of not less than 30% at the wavelength of 400 nm.

Brief Summary Text (20):
The porous membrane mentioned above can be produced by drying a coating film of a dope comprising a polymer, a good solvent for the polymer and a poor solvent for the polymer which has a higher boiling point than the good solvent.

Brief Summary Text (21):
The term "membrane" as used herein means a two-dimensional structure such as a thin [illegible] sheet or the like.

Detailed Description Text (2):
The porous membrane of the invention comprises a polymer and generally has a micro phase separation structure. This micro phase separation structure is formed by coagulation of a gel phase resulting from phase separation upon a change in composition of a flow-cast polymer solution. The configuration of the pores formed among particles are generally indefinite or amorphous, irregular, and non-circular or non-spherical.

Detailed Description Text (17):
Polysulfone-series Polymers

Detailed Description Text (18):
Polysulfones, polyethersulfones, etc.

Detailed Description Text (31):

At least [illegible] polymer [illegible] from the group consisting of cellulose derivatives, vinyl series polymers and [illegible] polymers is included among preferred polymers.

Detailed Description Text (4[illegible]):
The mean degree of substitution of the cellulose derivative can be selected within the range of about 1 to 3. For example, a preferred [illegible] acetylation of about 42 to 62% (e.g 43% to [illegible]%), preferably [illegible]. When the degree of substitution (degree of acetylation) is too low, the [illegible] is low. When the viscosity average degree of polymerization is too low, the [illegible] of the porous membrane becomes small or the membrane tends to become [illegible], whereas when it is too high, the pore size becomes large and the porous membrane tends to become opaque.

Detailed Description Text (42):
An outstanding feature of the present invention is that a membrane is highly transparent in spite that it is a porous membrane [illegible] having a micro phase-separation structure. Thus, the light transmittance of the porous membrane at the wavelength of 4[illegible] nm is not less than [illegible]%, preferably [illegible] preferably about [illegible] to [illegible]% (e.g. 55 to [illegible]%), especially about [illegible]%. Even porous membranes having a light [illegible] about [illegible] to [illegible]%, thus being highly transparent, can be [illegible].

Detailed Description Text (43):
The porous membrane has a maximum pore size of not larger than [illegible] .mu.m, in particular not larger than 0.4 .mu.m. The mean pore size is [illegible] 0.3 .mu.m, preferably about [illegible] to [illegible] .mu.m (e.g. [illegible]), and more preferably about 0.01 to 0.2 .mu.m (e.g. [illegible]).

Detailed Description Text (44):
Further, the porous membrane has a porosity of, for example, about [illegible] to [illegible]% (e.g. 15 to 50%), preferably about 15 to 55%, and more preferably about 2[illegible] to [illegible]%.

Detailed Description Text (45):
The thickness of the porous membrane is not critical but can be selected according to the intended use thereof. For example, it is about 1 to [illegible] .mu.m, preferably about 2 to 70 .mu.m, more preferably about 3 to [illegible] .mu.m. When the thickness is too small, the strength and water resistance will be insufficient. When it is too thick, the transparency may possibly be reduced in an application.

Detailed Description Text (4[illegible]):
The [illegible] of the present invention can be produced by the dry phase [illegible], namely by casting or applying a homogeneous dope containing a polymer, a good solvent for the polymer and a poor solvent for the polymer onto a substrate or support, and causing the solvents to evaporate to induce micro phase separation, although it can also be produced by another micro phase separation method, for example by the wet phase separation method comprising casting or applying a solution of a polymer in a good solvent onto a substrate, followed by immersion in a poor solvent for the polymer. In the dry phase conversion method, it is particularly important that, as the poor solvent, a solvent having a higher boiling point (high-boiling solvent) than the good solvent is used.

Detailed Description Text (48):
In the above dry phase separation process, the good and poor solvents should be selected with consideration for controlling the pore size of the porous membrane and attaining high transparency.

Detailed Description Text ([illegible]):
Good solvents for polysulfone-series polymers include [illegible] N,N-dimethylformamide, N,N-dimethylacetamide, etc., [illegible], and mixed solvents composed of these.

Detailed Description Text ([illegible]):
[illegible] preferred for acrylonitrile-series polymers, meth acrylic acid [illegible] polymers and polysulfone-series polymers include alkyl acetates which may have a C.sub.1-4 alkoxy group ([illegible] C.sub.1-4 alkoxy-C.sub.[illegible]-7 alkyl acetates such as 3-methoxybutyl acetate and [illegible]-methoxypentyl acetate, etc.), C.sub.4-8 alkoxy C.sub.1-4 alkyl alcohols such as [illegible] and [illegible], [illegible]

dialkyl ketones such as methyl butyl ketone, [illegible] ketone, [illegible] ketone and methyl isopentyl ketone, [illegible], and the like.

Detailed Description Text (62):
A conventional additive or additives may be added [illegible] an amount not to adversely affect the [illegible]. Examples of the additive including [illegible] [illegible] and [illegible] agents.

[illegible] Text [illegible]:
Although the substrate may be opaque or semitransparent, the substrate is generally transparent for effective utilization of the transparency of the porous membrane.

Detailed Description Text (67):
The plastic film may contain a conventional additive or additives, such as an antioxidant, ultraviolet absorber, heat stabilizer, lubricant, pigment, etc., when necessary. For improving the adhesiveness to the porous membrane, it may be subjected to corona discharge treatment or undercoat treatment, for instance.

Detailed Description Text (68):
In the process for producing the transparent porous polymer membrane according to the present invention, the first step is to coat the substrate with the dope which contains a polymer, a good solvent for the polymer and a poor solvent for the polymer having a higher boiling point than the good solvent.

Detailed Description Text [illegible]:
In the drying step for drying the dope thus applied, the [illegible] having a [illegible] boiling point evaporates preferentially. With the progress of this good solvent evaporation, the solubility of the polymer in the dope decreases and the polymer forms [illegible], resulting in phase separation from the poor solvent phase. With the further progress of drying, micelles contact with one another to form a network structure. Upon completion of the poor solvent evaporation, a porous membrane or porous film is formed.

Detailed Description Text (71):
After the drying step, the coating is peeled off from the substrate to give a highly transparent porous membrane or film. The porous membrane of the present invention is, in spite of being porous, highly transparent. The dry phase separation method contributes to the production of the highly transparent porous membrane at a high productivity.

Detailed Description Text (73):
The laminate film of the present invention has a porous membrane formed on at least one side of the above-mentioned substrate. This laminate film can be produced without peeling off the porous membrane formed on the substrate by the above method.

Detailed Description Text (74):
Furthermore, the laminate film of the present invention includes a laminate film comprising a pair of substrates and a porous layer interposed or sandwiched therebetween. Such a laminate film can be obtained by forming the porous membrane on one of the substrates and laminating another substrate on the porous membrane, if [illegible] intermediate adhesive layer.

Detailed Description Text (75):
The porous layer of the laminate film may be supplemented with a functional material such as liquid crystal molecules, an ionic conductor or a dichromatic coloring matter by immersion or dispersion, so that the resulting laminate film can be utilized as a functional film (e.g. liquid crystal film, conductive film, polychromatic polarizing plate). When the above-mentioned transparent porous membrane is laminated on a metallic reflector, the resulting laminate film can be utilized as an optically interfering film, which gains color by interference of light.

Detailed Description Text (76):
Since the porous membrane of the present invention is excellent in transparency, it can be used in a variety of fields where transparency is required, for example as an element for crystal optics or optical elements, a recording sheet, a functional film material, a separation membrane, or an analytical element [illegible] or the like. By way of example, when the porous membrane or film is applied [illegible]

image-accepting layer of a recording sheet for use in an ink jet recording system or the like, the absorption of ink can be improved.

Detailed Description Text (50):
The ink absorbing layer formed on at least one side of the above-mentioned [illegible] not particularly limited, provided that it comprises a material capable of [illegible] ink. The ink-absorbing layer can be composed of a polymer. The polymer includes [illegible] ethers, naturally-occurring polymers or derivatives thereof, cellulose derivatives, olefinic polymers, acrylic polymers, styrenic polymers, vinyl series polymers, vinyl acetate-series polymers, vinyl ether-series polymers, etc., vinyl alcohol [illegible] polymers, polyalkylene oxides, polyesters, polyamides, polycarbonates, polyurethanes, polysulfones, and epoxide-derived polymers. These polymers may have hydrophilic [illegible] (acidic groups such as carboxyl and sulfo groups or salts thereof, [illegible] salts thereof.

Detailed Description Text (114):
As the hydrophilic polymer, use can be made of the polymers mentioned above hydrophilic polymers as exemplified in connection with the ink-absorbing layer, [illegible] porous membrane. The hydrophilic polymer includes, more specifically, [illegible] (meth)acrylonitrile-series polymers, [illegible] derivatives, vinyl-series polymers (meth)acrylic polymers, polyvinylpyrrolidone, polyvinyl acetate and completely or partially saponified products thereof (polyvinyl alcohol, etc.), ethylene-vinyl acetate copolymers and completely or partially saponified products thereof, polyalkyl vinyl ethers, carboxyl group containing polymers or salts thereof, etc.), polyalkylene oxides (polyethylene glycol, etc.), polyamides, polyethyleneimine, polysulfones, polyethersulfones, etc. These hydrophilic polymers may be used alone or in combination of two or more.

Detailed Description Text (153):
A coating composition (dope) was prepared by adding 2.6 parts by weight of 1,2-diethoxyethane to 100 parts by weight of a 15% (by weight) solution of a polysulfone ("P-1700", product of Udel Co.) in 1,4-dioxane with thorough stirring. The coating composition was applied to a PET film coated with polyvinyl alcohol, in an amount sufficient to give the resulting film a thickness of [illegible] .mu.m. The coated film was dried at 25 degree. C. and 95% RH for 5 minutes and further dried at 1[illegible] degree. C. for 3 minutes.

Detailed Description Text (168):
A dope was prepared by adding 15 parts by weight of 3-methoxybutyl acetate to 100 parts by weight of a 14% (by weight) solution of a polyethersulfone (product of Sumitomo [illegible] Ltd.) in N,N dimethylformamide with thorough stirring. The dope was [illegible] paper in such a manner as to give, when dried, a coating of 3[illegible] .mu.m. The coated paper was dried at 6[illegible].degree. C. and 95% RH for 1.5 minutes and then at 120.degree. C. for 3 minutes. The film peeled off from the release paper was a porous film having a mean pore size of 0.05 .mu.m and a porosity of 30%. The light transmittance was 80%, indicating high transparency of the film.

Detailed Description Text (183):
A 15 .mu.m thick ink-absorbing layer was formed on a 100 .mu.m thick polyethylene terephthalate film (Melinex 705; product of ICI Japan) which was already treated for facilitating adhesion, by applying thereto a 15% (by weight) aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G; product of Nippon Synthetic Chemical Industry Co., Ltd.), followed by drying at 12[illegible].degree. C. for 3 minutes. A coating composition (dope) was prepared by adding 45 parts by weight of cyclohexanone to 100 parts by weight of an 8% (by weight) solution of cellulose acetate (mean degree of acetylation 55, viscosity average degree of polymerization 17[illegible]) in methylene [illegible]. This coating composition was applied onto the ink-absorbing layer and dried in an atmosphere of a temperature of 35.degree. C. and a humidity of [illegible]% RH for [illegible] minutes and then at 120.degree. C. for 3 minutes, to give a white porous membrane having a mean pore size of 1.1 .mu.m, a porosity of [illegible]% and a thickness of [illegible] .mu.m.

Detailed Description Text ([illegible]):
A [illegible] ink-absorbing layer was formed on a 1[illegible] .mu.m thick polyethylene terephthalate film (Melinex 7[illegible]; product of ICI Japan) already treated for facilitating adhesion, by applying thereto a 15% (by weight) aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G, product of Nippon Synthetic Chemical Industry Co., Ltd.), followed by 3 minutes of drying at 12[illegible].degree. C. A coating composition (dope) was prepared by adding 15 parts by weight of 3-methoxybutyl acetate to 100 parts by weight of a 14% (by weight) solution of a polyethersulfone (P48[illegible], product of Sumitomo

Chemical Company Ltd., in N,N-dimethyl[illegible] was applied onto the [illegible] composition was applied [illegible] .degree. C. and a humidity of [illegible]% RH for [illegible] minutes, to give a porous layer having a mean [illegible] [illegible]% and a thickness of [illegible] .mu.m.

[illegible]

1. A porous membrane comprising at least one polymer selected from the group consisting of cellulose derivatives, vinyl-series polymers and polysulfone-series polymers, and showing a light transmittance of not less than [illegible]% at the wavelength of [illegible] nm.

2. A porous membrane as claimed in claim 1 which has a micro phase separation structure

3. A porous membrane as claimed in claim 1 which has pores having a mean pore size of 0.002 to 0.35 .mu.m, with the maximum pore size of not larger than [illegible] .mu.m.

4. A porous membrane as claimed in claim 1 which has a porosity of 15 to [illegible]%.

5. A porous membrane as claimed in claim 1, wherein said polymer is at least one polymer selected from the group consisting of cellulose esters, (meth)acrylonitrile-series polymers, (meth)acrylic acid ester-series polymers and polysulfone-series polymers.

6. A porous membrane as claimed in claim 1, wherein said polymer is at least one member selected from the group consisting of:

[illegible] with a degree of acetylation of 42 to 62% and a viscosity average [illegible] degree of [illegible];

(b) homopolymers or copolymers obtainable from a monomer selected from the group consisting of (meth)acrylonitrile, (meth)acrylic acid ester-series monomers, vinyl ester-series monomers, heterocyclic vinyl-series monomers, aromatic vinyl monomers, and polymerizable unsaturated dicarboxylic acids or derivatives thereof; and

(c) at least one member selected from the group consisting of polysulfone and polyethersulfone

7. A porous membrane (A) comprising at least one polymer selected from the group consisting of cellulose derivatives, vinyl-series polymers and polysulfone-series polymers, (B1) having a porosity of 10 to 60% or (B2) having pores with a mean pore size of 0.002 to 0.35 .mu.m and a maximum pore size of not larger than 0.4 .mu.m, and (C) showing a light transmittance of not less than 30% at the wavelength of 400 nm.

8. A porous membrane as claimed in claim 7, wherein the light transmittance is not less than 50%.

9. A laminate film which comprises a substrate and a porous layer formed on at least [illegible] of said substrate, said porous layer comprising at least one polymer selected [illegible] consisting of cellulose derivatives, vinyl-series polymers and [illegible] polymers and having a light transmittance of not less than 30% at the wavelength of [illegible] nm.

10. A laminate film which comprises a plurality of substrates and a porous layer interposed or sandwiched between said substrates, said porous layer comprising at least one polymer selected from the group consisting of cellulose derivatives, vinyl-series polymers and polysulfone-series polymers and having a light transmittance of not less than 30% at the wavelength of 400 nm.

11. A process for producing porous membranes recited in claim 1, which comprises drying a coating layer or film of a dope comprising a polymer, a good solvent for the polymer and a poor solvent for the polymer, said poor solvent having a higher boiling point than the good solvent.

12. A process for producing porous membranes as claimed in claim 11, wherein said [illegible] comprises a polymer, at least one good solvent selected from the group [illegible] ketones, esters, ethers, [illegible] halogenated hydrocarbons, [illegible]

solvent having a boiling point of 35 to 2[illegible].degree. C., and at least one poor solvent selected from the group consisting of esters, alcohols, ketones, ethers and aliphatic hydrocarbons, said poor solvent having a boiling point of 1[illegible] to 2[illegible].degree. C.

13. A process for producing porous membranes as claimed in claim [illegible], wherein [illegible] comprises at least one good solvent selected from the group [illegible] C.sub.1-4 alkyl acetates, [illegible] C.sub.1-4 alkyl ketones, [illegible] C.sub.1-4 alkyl [illegible] alkyl [illegible], [illegible] alkylamides, di-C.sub.1-3 alkyl sulfoxides and [illegible] alkyl [illegible], and at least one poor solvent selected from the group consisting of [illegible] alkyl-C.sub 2-4 aliphatic carboxylates which may have a C.sub.1-4 alkoxy group, [illegible] C.sub.1-4 alkyl benzoates, C.sub.4 - cycloalkanols which may have an alkyl group, [illegible] C.sub.2-[illegible] alkoxy-C.sub.1-4 alcohols, [illegible] dialkyl ketones, [illegible] and C.sub 5-20 aliphatic hydrocarbons.

14. A process for producing porous membranes as claimed in claim 11, wherein the [illegible] points between the good solvent and the poor solvent is 2 to [illegible]

15. A process for producing porous membranes as claimed in claim 11, wherein the drying is carried out first at a temperature of 10 to 100.degree. C. and a relative humidity of 50 to 90% for 30 seconds to 60 minutes and further at a temperature higher than said temperature for 2 seconds to 30 minutes.

16. A process for producing porous membranes as claimed in claim 11, wherein the proportion of the poor solvent is 1 to 50 parts by weight per 100 parts by weight of the good solvent.

17. A process for producing porous membranes as claimed in claim 11, wherein said dope contains 3 to 40 parts by weight of the poor solvent per 100 parts by weight of a 5 to 30% (by weight) solution of said polymer in the good solvent.

18. A recording sheet which comprises a substrate, an ink-absorbing layer formed on at least one side of said substrate, and a porous polymer layer having a micro phase-separation structure formed on said ink-absorbing layer, wherein said porous polymer layer comprises at least one polymer selected from the group consisting of cellulose derivatives, vinyl-series polymers and polysulfone-series polymers.

[illegible] A porous membrane produced by a process comprising drying a coating layer or film comprising at least one polymer selected from the group consisting of cellulose derivatives, vinyl series polymers and polysulfone-series polymers, a good solvent for the polymer and a poor solvent for the polymer, wherein the poor solvent having a higher boiling point than the good solvent and the proportion of the poor solvent is 1 to 50 parts by weight per 100 parts by weight of the good solvent, and which shows a light transmittance of not less than 30% at the wavelength of 4[illegible] nm and has a micro phase separation structure and a mean pore size of [illegible] 2 to [illegible] .mu.m. with the maximum pore size of not larger than 0.4 .mu.m.

21. A porous membrane as claimed in claim 6, wherein said homopolymer or copolymer [illegible] is obtainable from a monomer selected from the group consisting of (meth)acrylonitrile and (meth)acrylic acid ester-series monomers.